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18 separate items enclosed

NOTIFIE[redacted]

10/1CA9F

MEMORANDUM FOR PR (In-House Publication)

FROM: PROI (TI) (STINFO)

30 November 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-1999-0229**
Phillips, S., et al., "Hybrid POSS Polymer Technology for Rocket & Space Applications" (BFI)

49th JANNAF Propulsion Meeting (Tucson, AZ, 14-16 Dec 1999) **(Statement A)**

"Hybrid POSS Polymer Technology for Rocket & Space Applications"

JANNAF December 1999

Dr. Shawn H. Phillips
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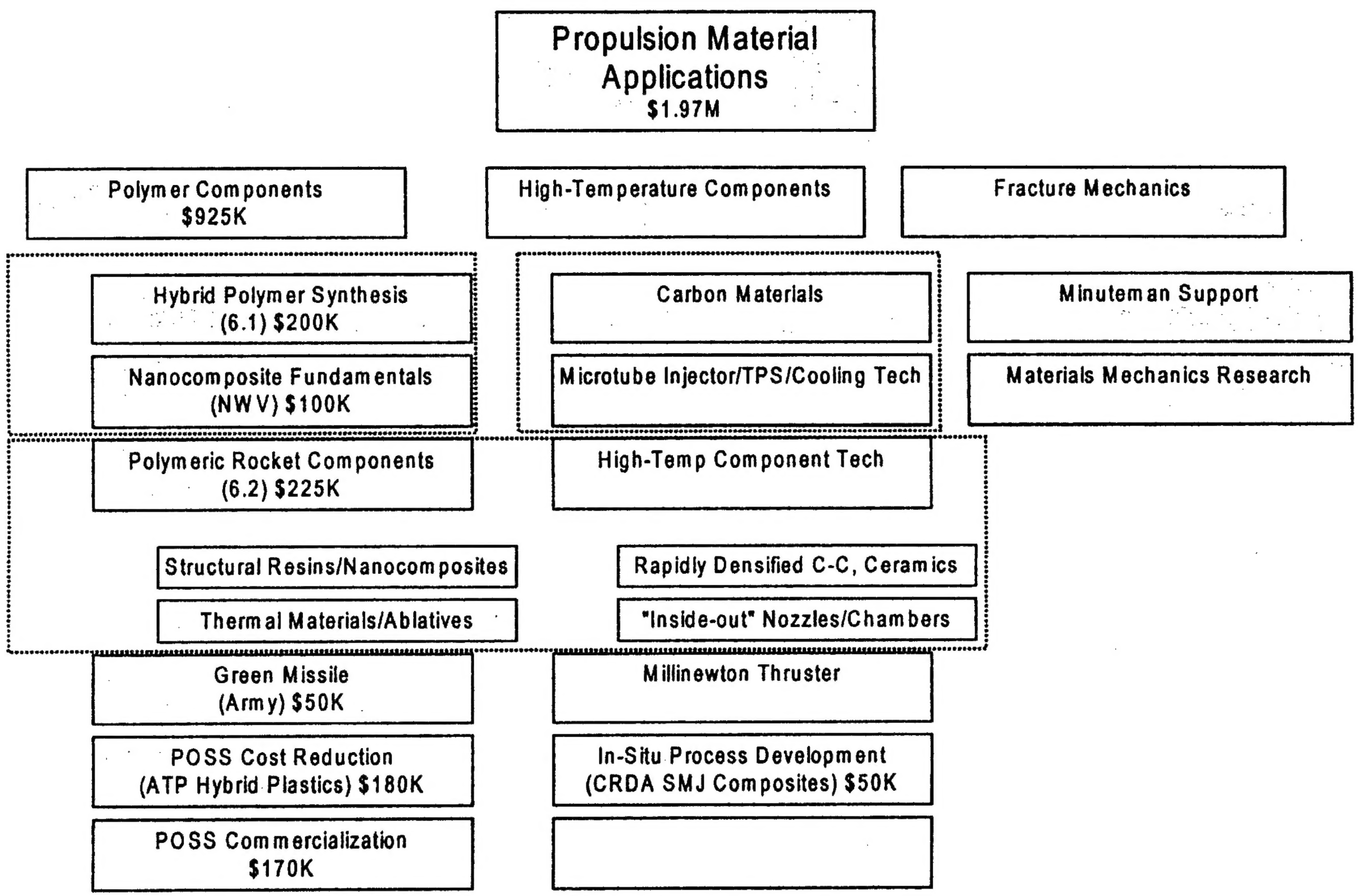
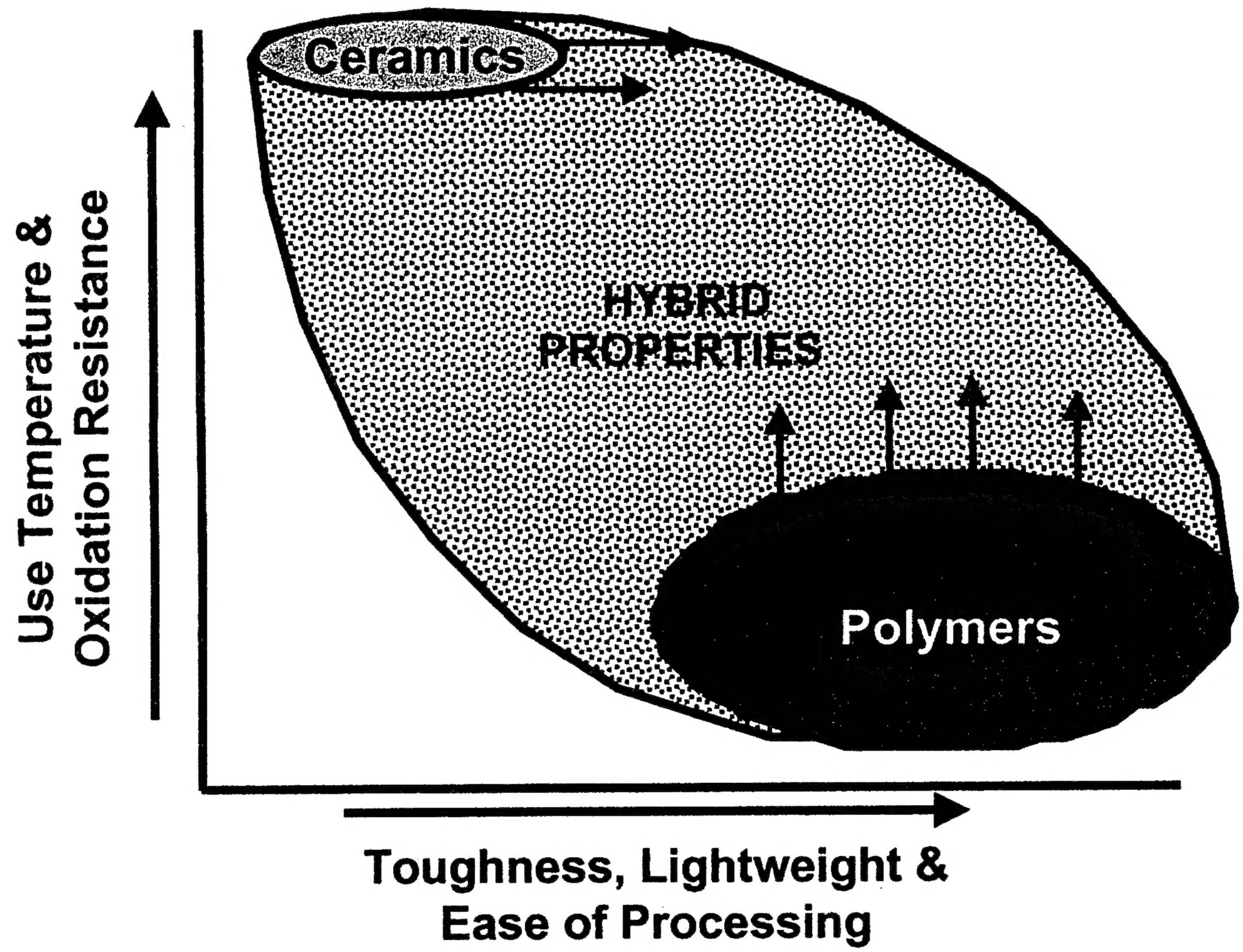
Propulsion Sciences Division
Edwards Air Force Research Lab

PRSM Work Breakdown Structure



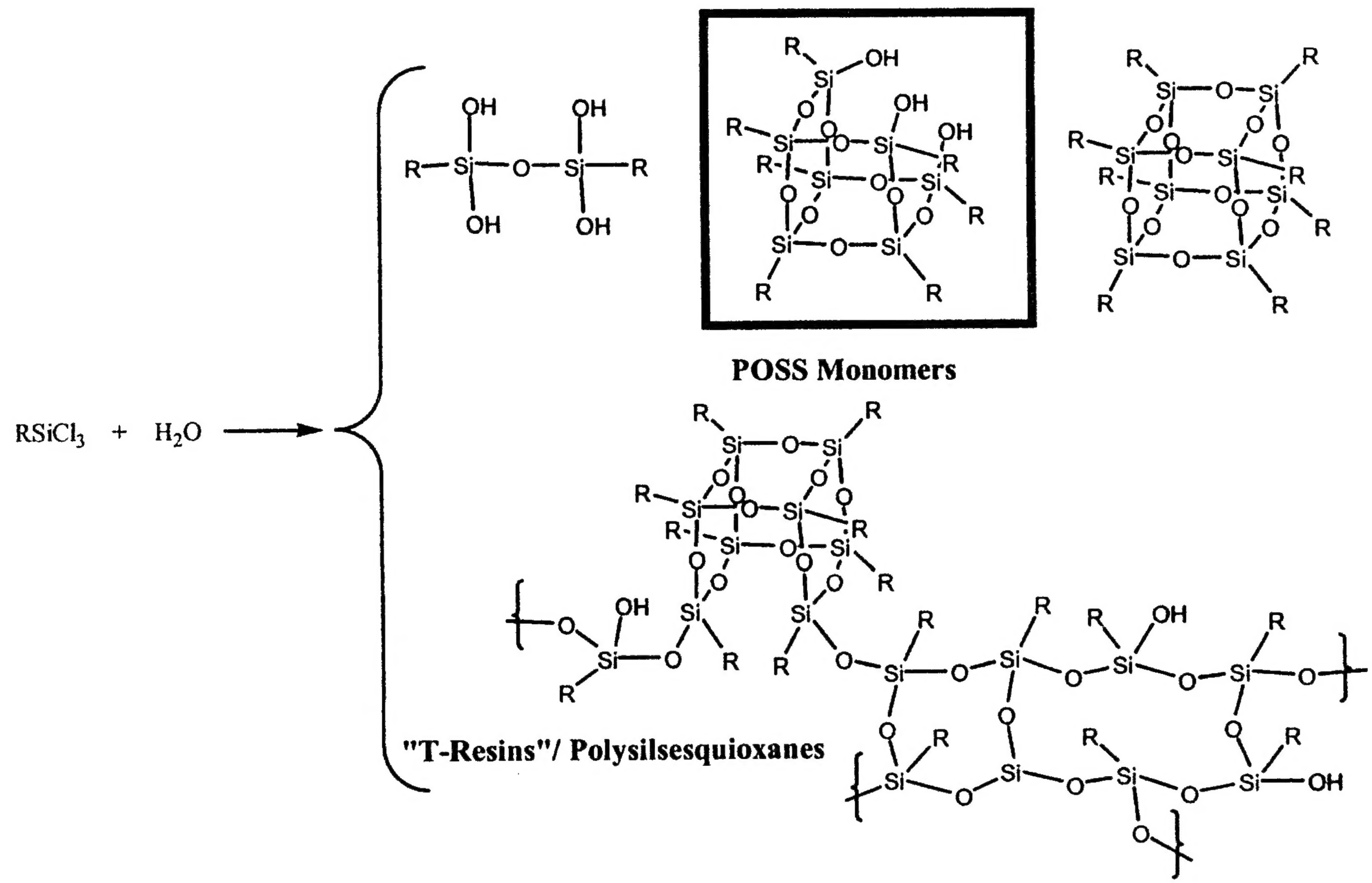
Propulsion (Air Force) Technology is Limited by Material Properties

Goal: Develop High Performance Polymers that REDEFINE material properties



•Hybrid plastics can bridge the barrier between ceramics and polymers

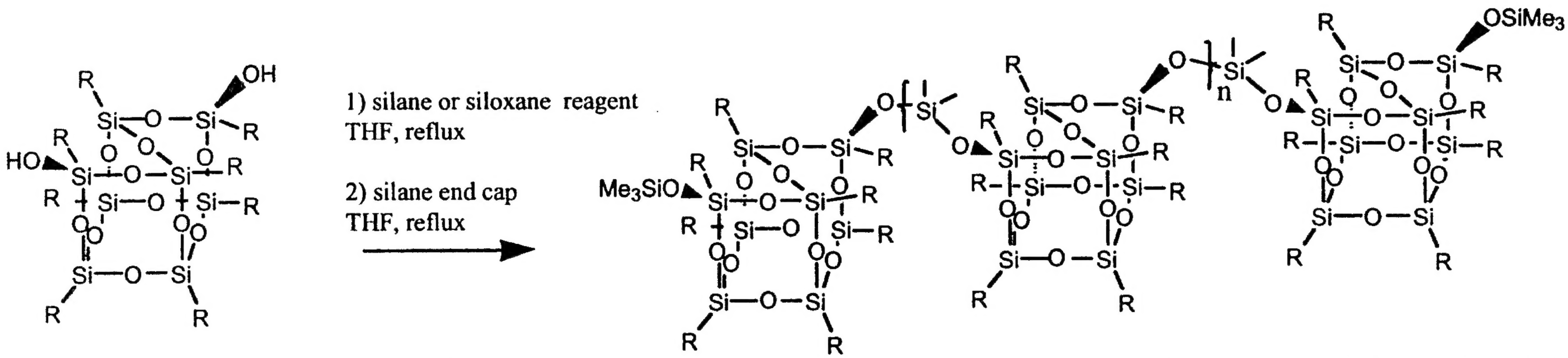
POSS = Polyhedral Oligomeric Silsesquioxane

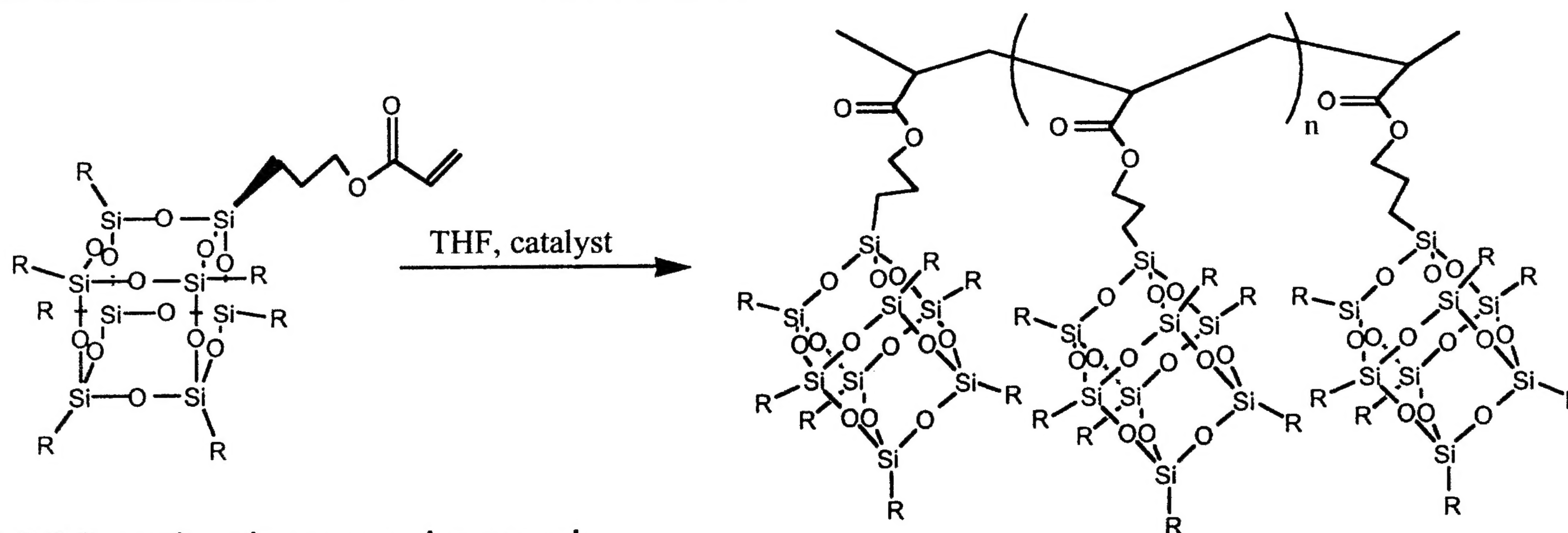


- Traditional silsesquioxane chemistry focused on "T-Resins"
- The maximization of property enhancements in polymers results from interaction at the nano-level (Edwards AFRL/PRSM ---> POSS monomers)

POSS-Based Hybrid Polymers

POSS-macromers can be employed in the same manner as “common” organics





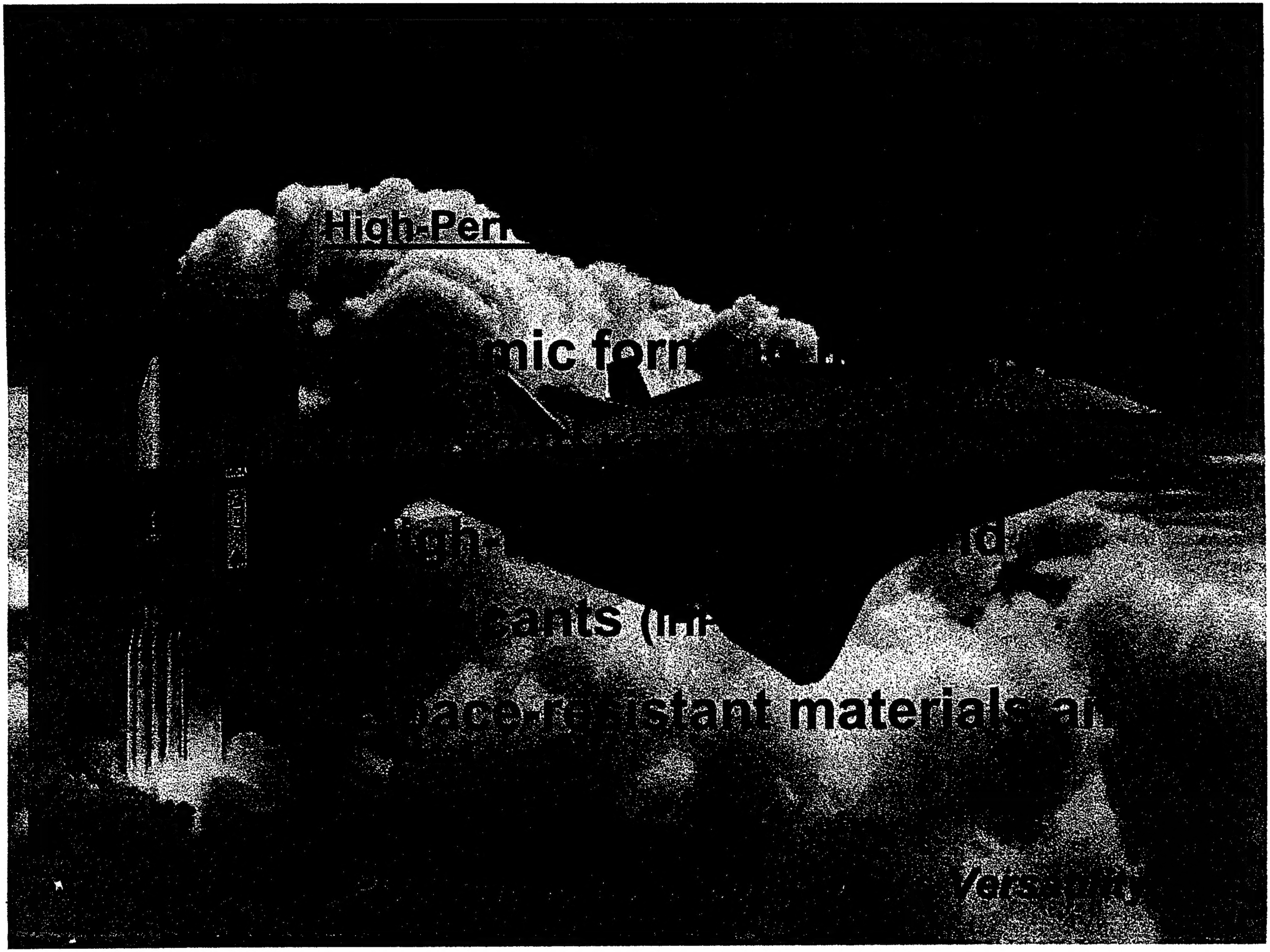
POSS-technology can be used in either monomer or polymer form.

Lichtenhan et. al. *Macromolecules* **1993**, *26*, 2141
Lichtenhan et. al. *Macromolecules* **1995**, *28*, 8435
Lichtenhan. *Comments on Inorganic Chemistry*, **1995**, *17*, 115

Property Enhancements via POSS

Observed in POSS-Copolymers and Blends

increased T_g	increased T_{dec}	enhanced blend miscibility
reduced flammability	extended temperature range	oxidation resistance
reduced heat evolution	increased oxygen permeability	altered mechanicals
lower density	lower thermal conductivity	reduced viscosity
disposal as silica	thermoplastic or curable	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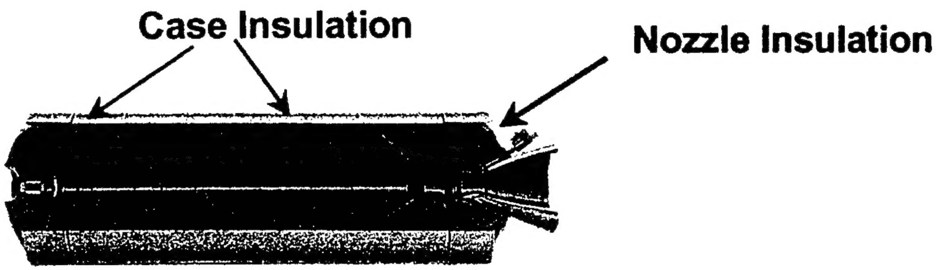
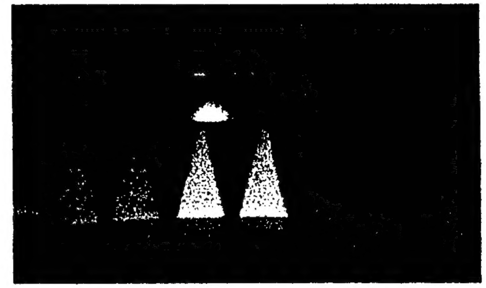
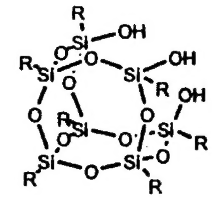
Solid Rocket Motor Nozzle Insulation





Char Motor Polymer Insulation Samples



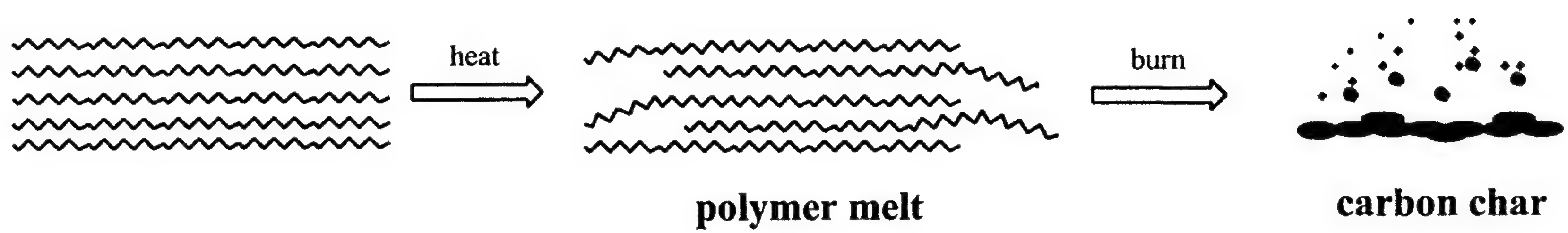
Goal: 50% Lower Erosion of Insulation (44 % weight reduction, 7.4% booster payload increase) – Phase III IHPRPT
Objective: Development of Ceramic Forming Polymer

Technical Challenges:

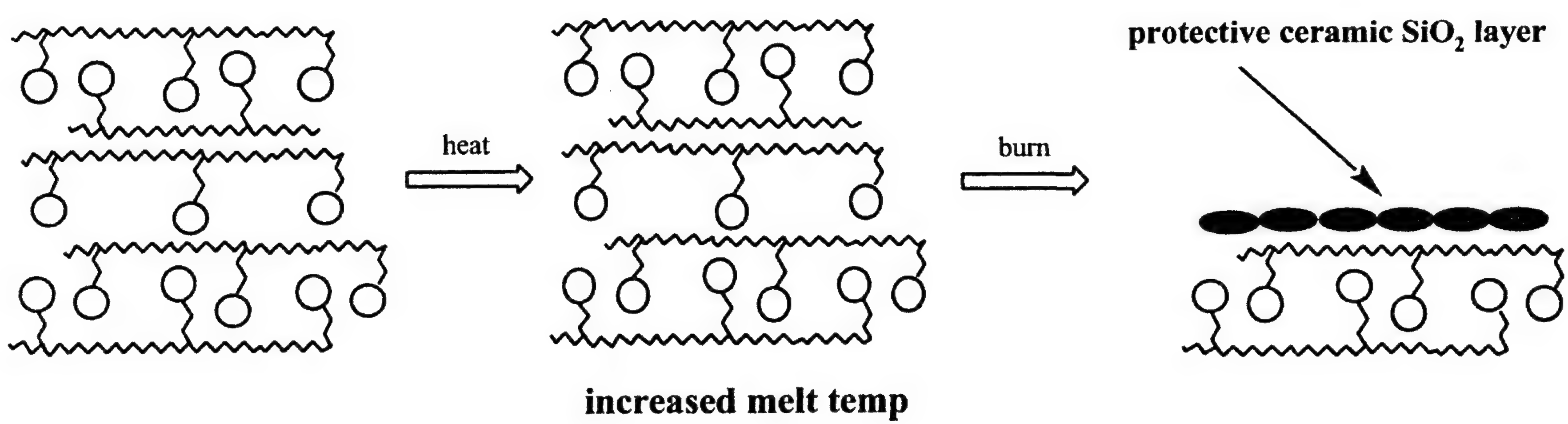
- Development/modification of insulation chemistry to incorporate pre-ceramic polymers
- Char formation/erosion under different operational conditions/prediction capabilities
- Achieving good adhesion and physical properties at the insulation/case interface

POSS for Flame Retardant Materials

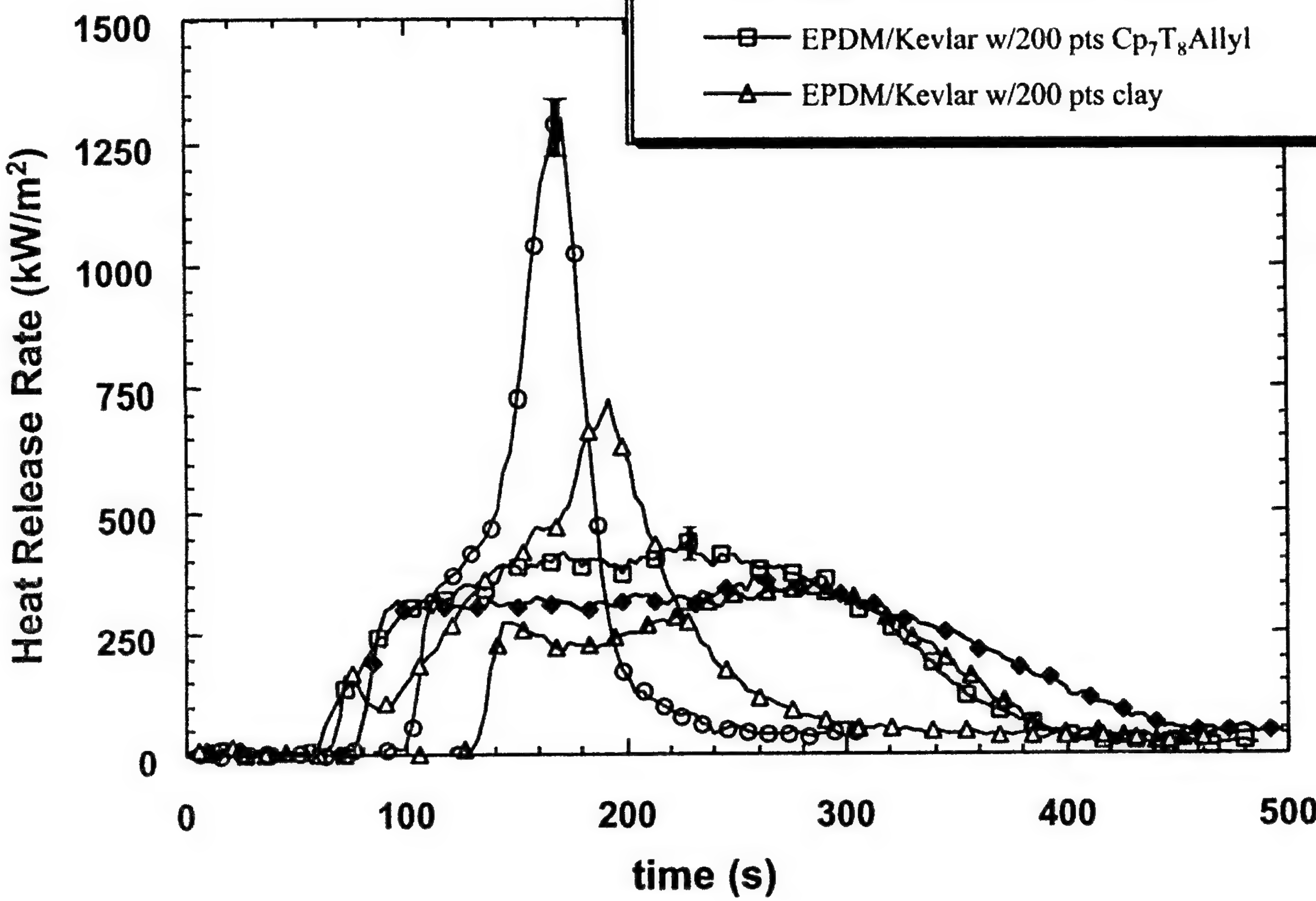
Traditional Polymer

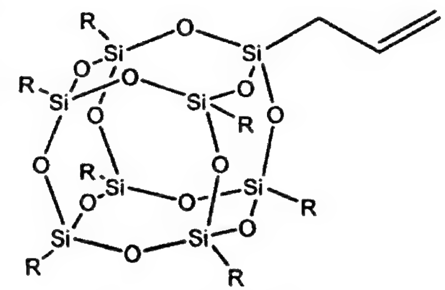


POSS Polymer

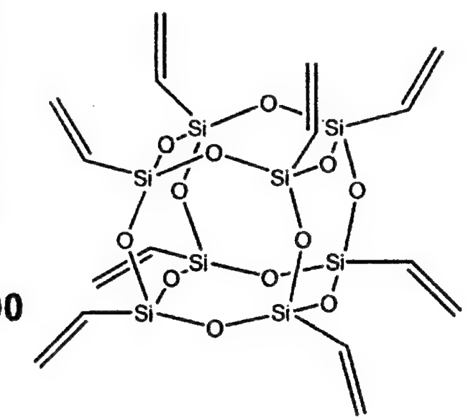


Cone Calorimeter Data

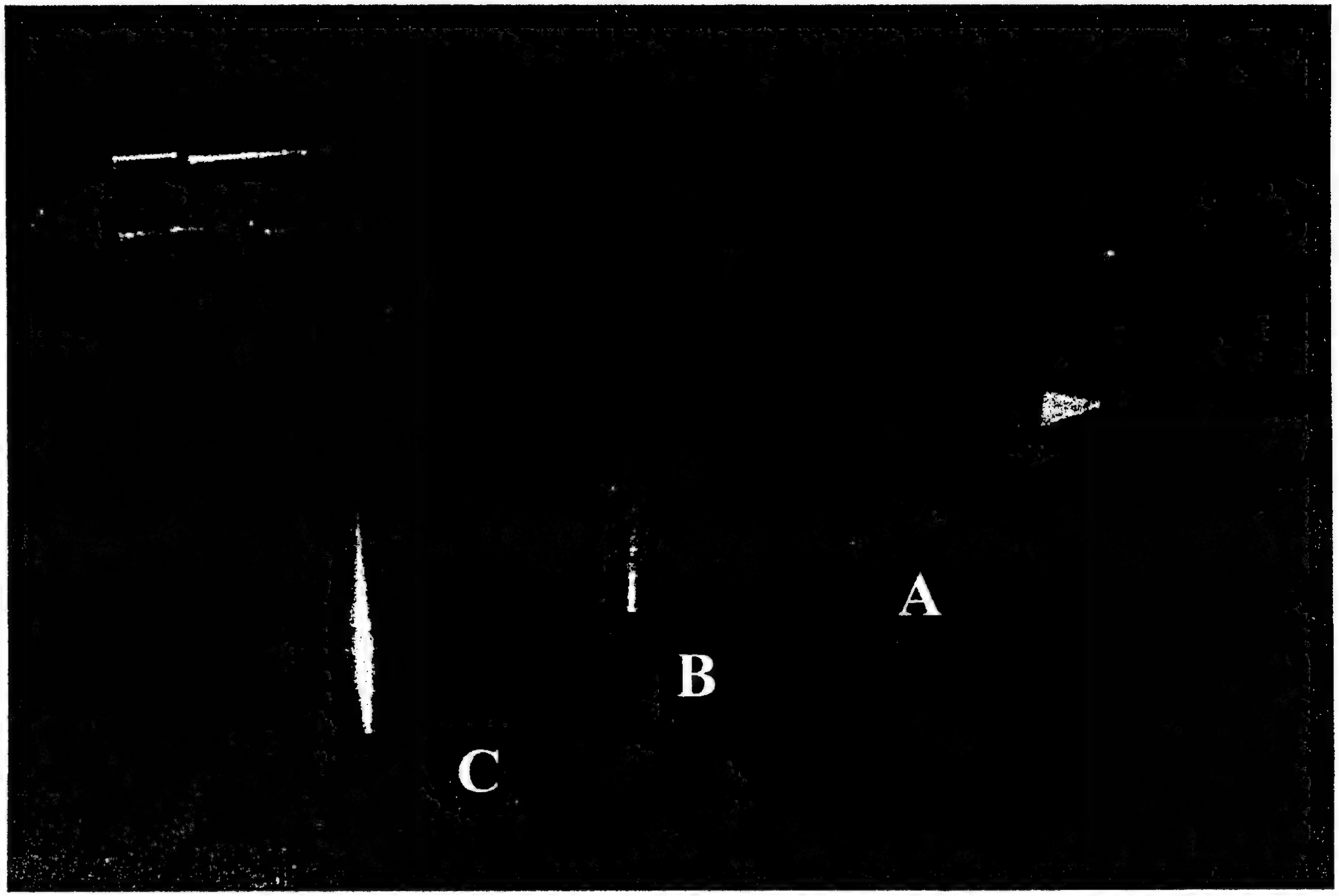




R = cyclopentyl



Solid Rocket Motors Insulation



A) Insulation containing POSS monomers
B) Convergent Cone
C) Convergent Cone + Insulation

Convergent Cone SRM Insulation Tests

Propellant			XXXX			XXXXX		
Ave Pressure			1340 psi			1310 psi		
Duration			6.5 sec			6.3 sec		
Insulation /Filler			[redacted]	POSS-Allyl (25%)	POSS-Octavinyl (25%)	[redacted]	Poss-Allyl (50%)	Poss-Octavinyl (50%)
Stn No.	e	Ma No.	[redacted]	%Ablated Depth	%Ablated Depth	[redacted]	%Ablated Depth	%Ablated Depth
0	3.5	.17	[redacted]	200	154	[redacted]	350	100
1	4.0	.15	[redacted]	115	121	[redacted]	200	111
2	6.6	.09	[redacted]	100	123	[redacted]	100	85
3	9.8	.06	[redacted]	100	100	[redacted]	200	137
4	13	.05	[redacted]	100	100	[redacted]	200	60
5	21	.03	[redacted]	100	100	[redacted]	100	-300
6	33	.02	[redacted]	100	100	[redacted]	-200	-500
7	47	.01	[redacted]	100	100	[redacted]	-500	-750

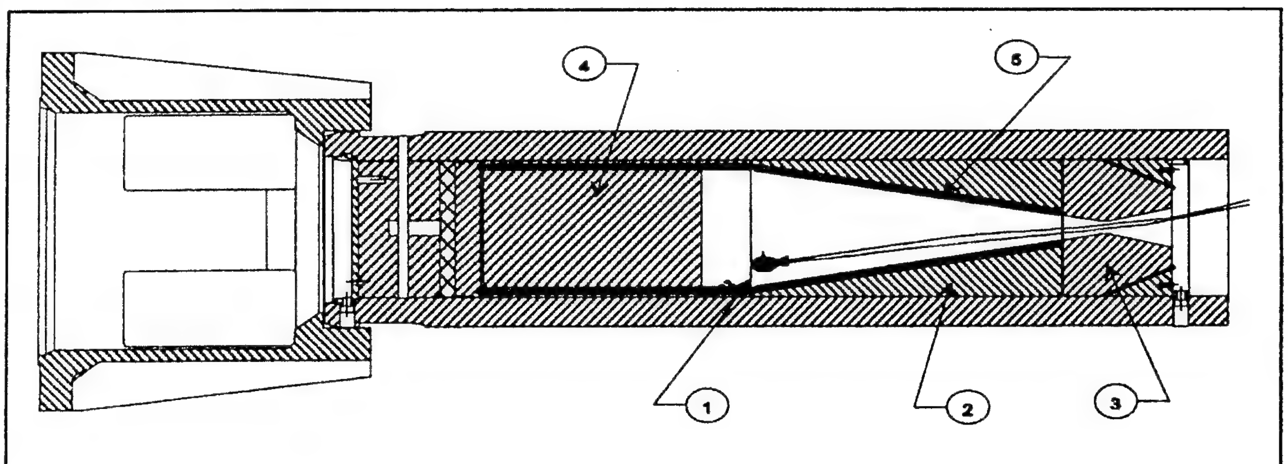
Negative numbers represent the formation of a structural char

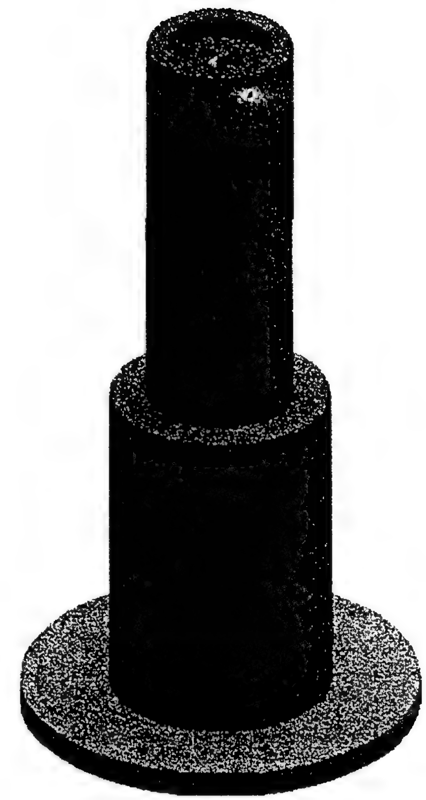
In-House SRM Insulation Testing

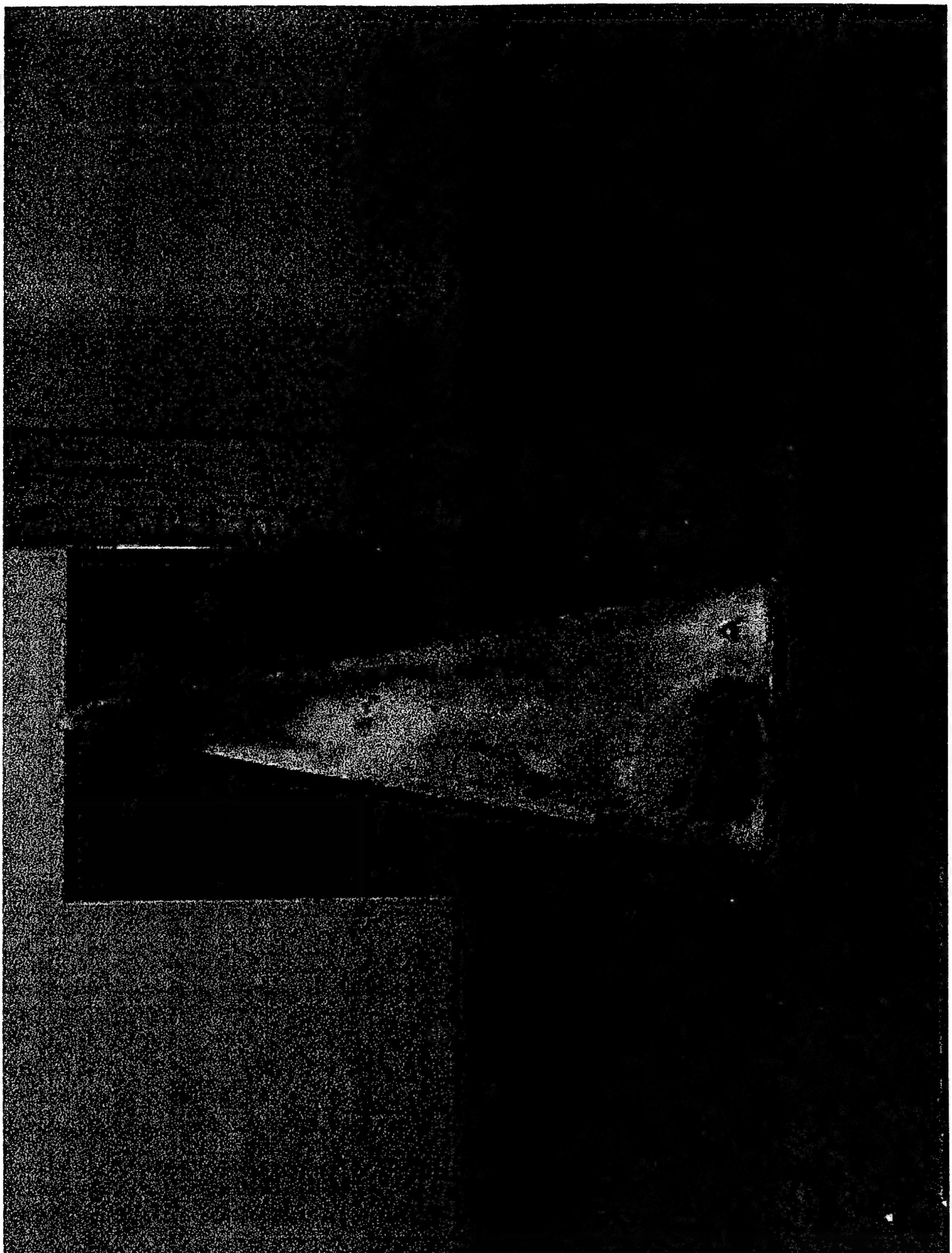
Objective: Los Cost/Low Volume Screening of New Materials for Rocket Motor Insulation

Capabilities:

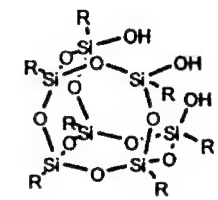
- Test facilities developed at Edwards AFRL (2 ¾" Pi-K Motor)
- Volume of material reduced from 5 Kg to 75 g
- Cost (synthesis, part fabrication, ablation test, analysis) reduced to 1K!!
- Rapid testing of 5-6 samples per day.







Solid Rocket Motors Insulation



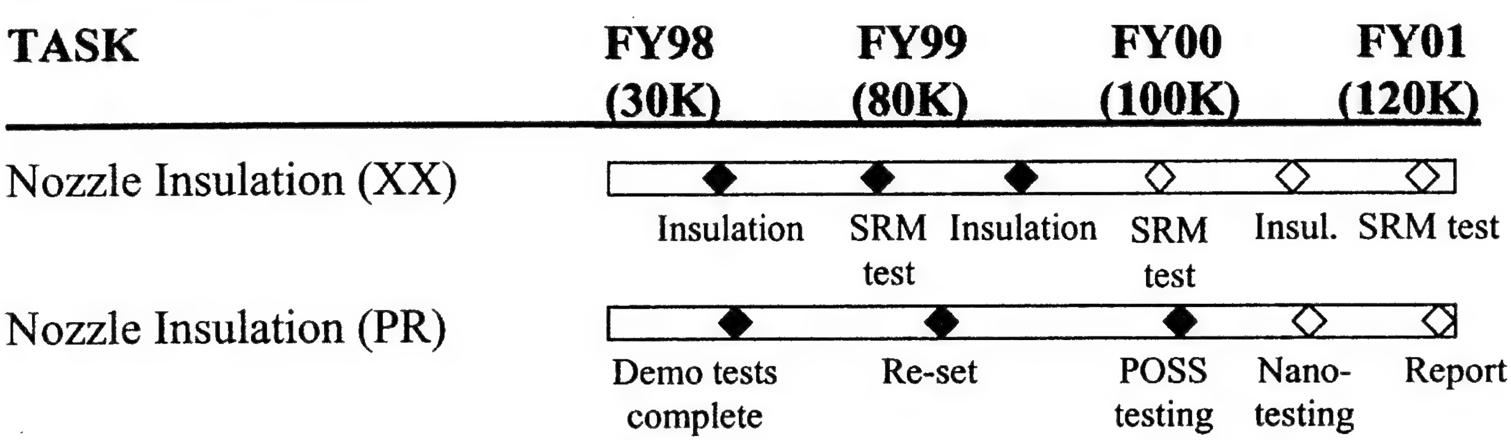
FY99 Accomplishments:

- 25% weight reduction & ceramic layer formed (industrial testing)
- Restart of small rocket motor testing, Area 1-30
- Organization of 30 lb. synthesis of POSS monomers from HP

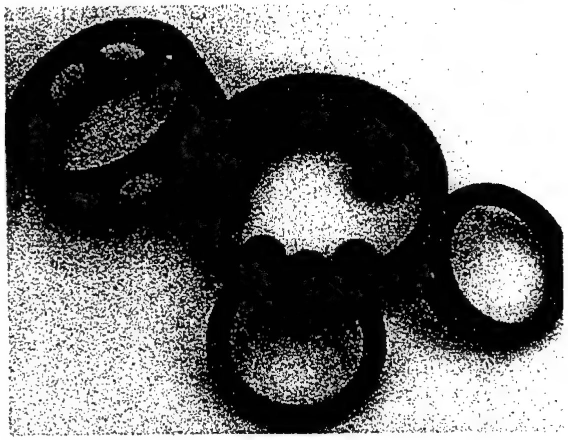
FY00 Objectives:

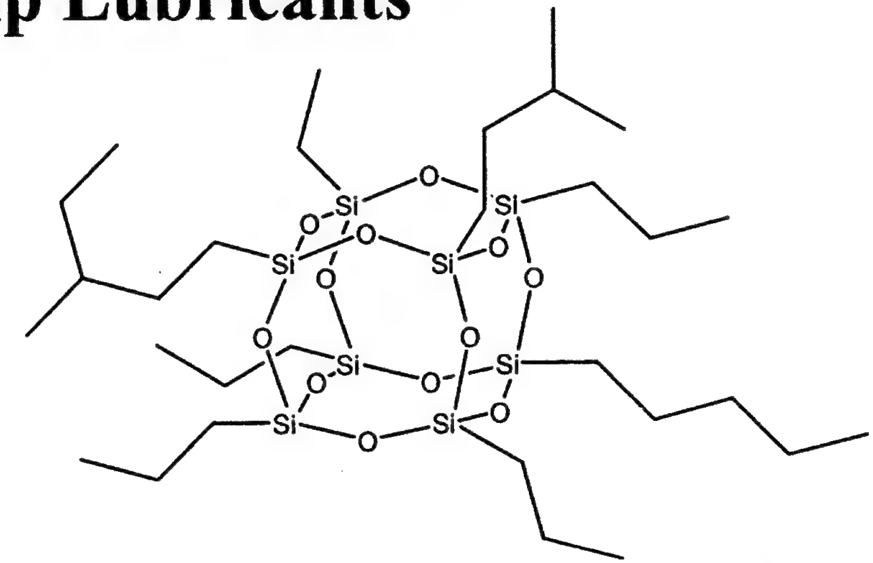
- Incorporation of POSS monomers into insulation
- 8 large-scale rocket motor firings with industrial partner (binding mode, monomer type, ablation & loading maximum)
- 30 small SRM tests utilizing metal oxides nanopowders & POSS
- modeling simulation of nanoparticle aggregation (NIST)

Tasks/Schedules:



High Temp Lubricants



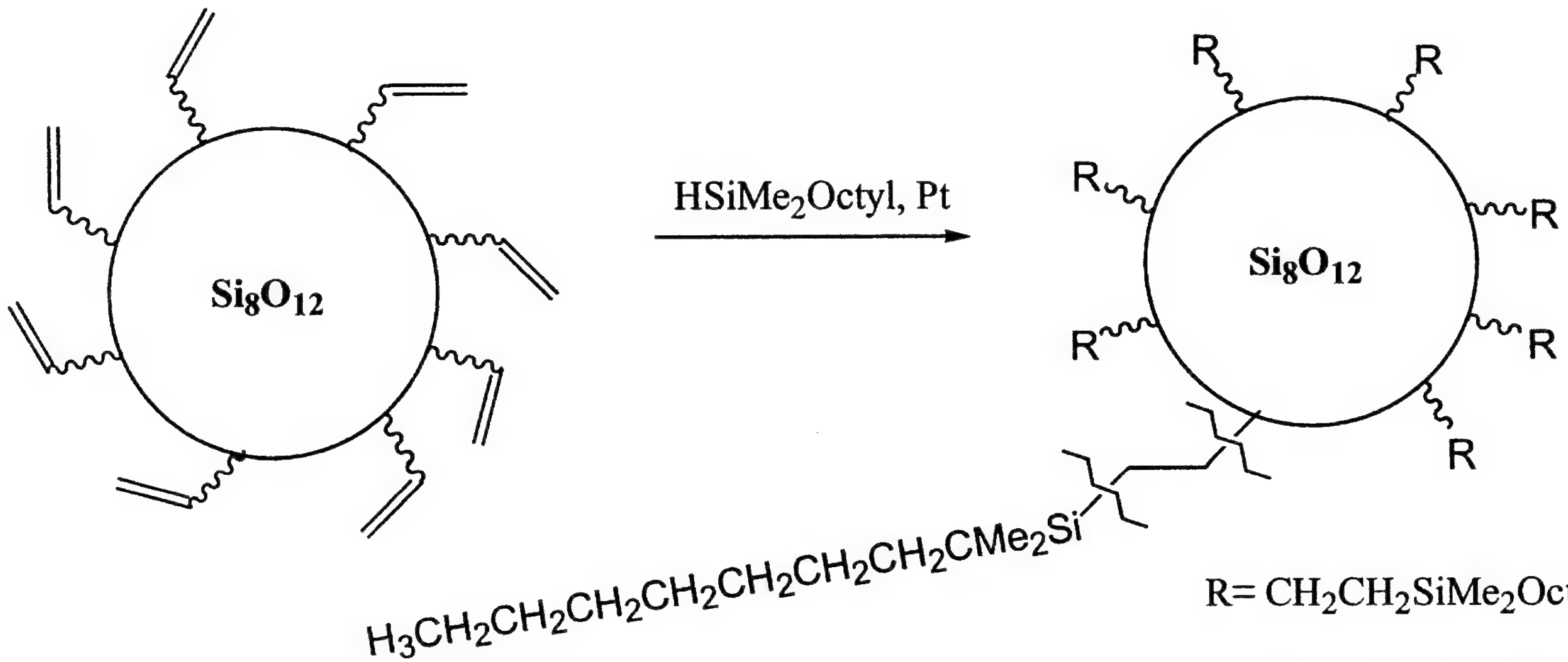


Goal: Replace ester-based lubricant with modified POSS lubricant.

Objectives:

- Fluid with working temperature range of -40° to 600° F (IHPTET)
- Ester lubricants limited to 400 °F: POSS monomer T_{dec} = 590 °F
- 600 °F lube = 1.5-1.6 T/W improvement

Generation I POSS Lubes

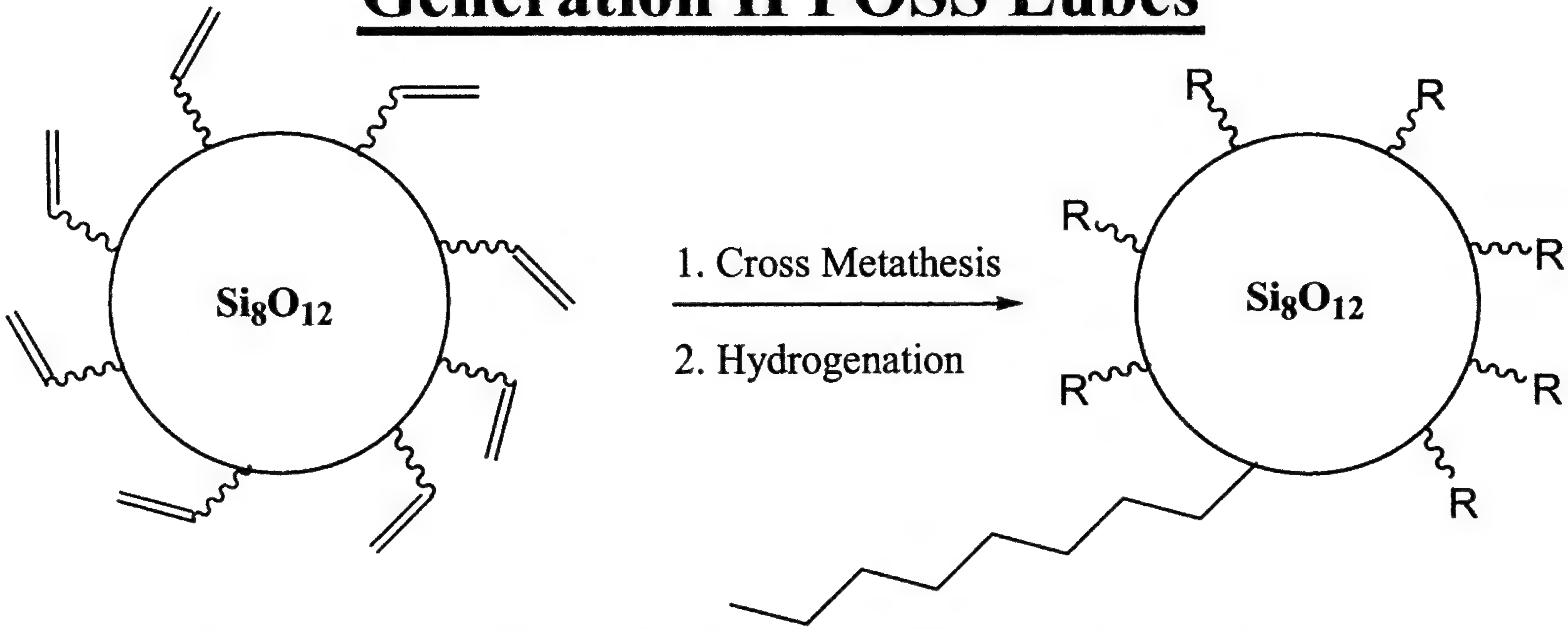


R= $CH_2CH_2SiMe_2Octyl$

OIL AT Room Temp.
T_{dec} low (< 200 °C)

This class is NOT suitable for High Temp Lubes, but may be suitable for blendables

Generation II POSS Lubes



Decomposition of POSS Lubes – TGA Data

Reagent	mp °C	iso temp °C	time for 10% loss (min)	% lost over 9 hours
Grade 4 Base stock	liq	219	30	90
$T_8(CH_2CH_2SiMe_2Octyl)_8$	liq	218	41	39
$T_8(octyl)_7(ethyl)_1$-grease	45	216	225	11
$T_8(octyl)_8$-solid	50	218	60	27
Cy_2T_2 $(OSiMe_2Octyl)_4$	liq	219	evaporated	100 (evap)

Decomposition of Lubricants

Three Ball and Disk Test for Selected Lubes

Table 4. 75°C TBOD wear test results
(0.5-mL sample, 246 rpm, 20-kg load, M50 balls and disk, 3-hour tests)

Test Fluid	Additive (concentration)	Average COF	Wear Scar Length (mm)
Gen I POSS*	TCP (2%)	0.205 ± 0.022	4.132
O-86-2 basestock	-	0.100 ± 0.007	0.868
O-86-2 basestock	$T_8Octyl_7Et_1$ (5%)	0.138 ± 0.010	0.701
O-86-2 basestock	T_8Octyl_8 (5%)	0.118 ± 0.011	0.645
O-86-2 basestock	$CyT_2(octyl)_4$(5%)	0.109 ± 0.006	0.581

*Test was suspended after 1 hour

Merging Technical Issues:

- Control viscosity of POSS lubes (-40° to 600° F)

- Decomposition of POSS lubes to silicate core (sand)

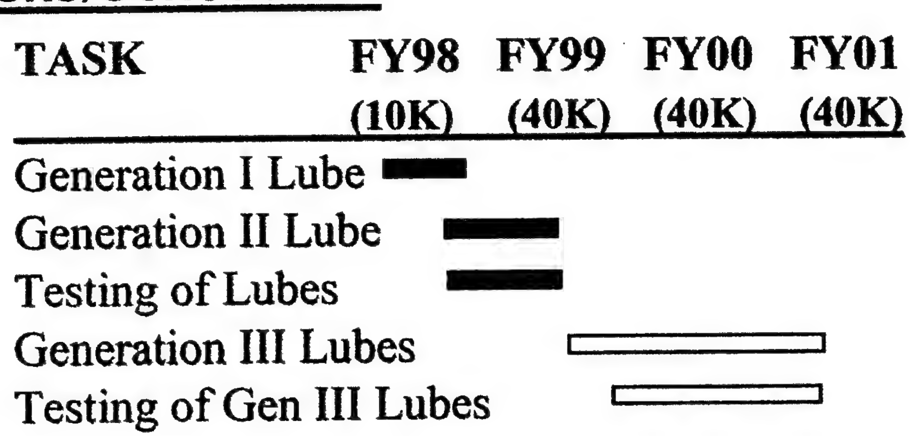
FY99 Accomplishments:

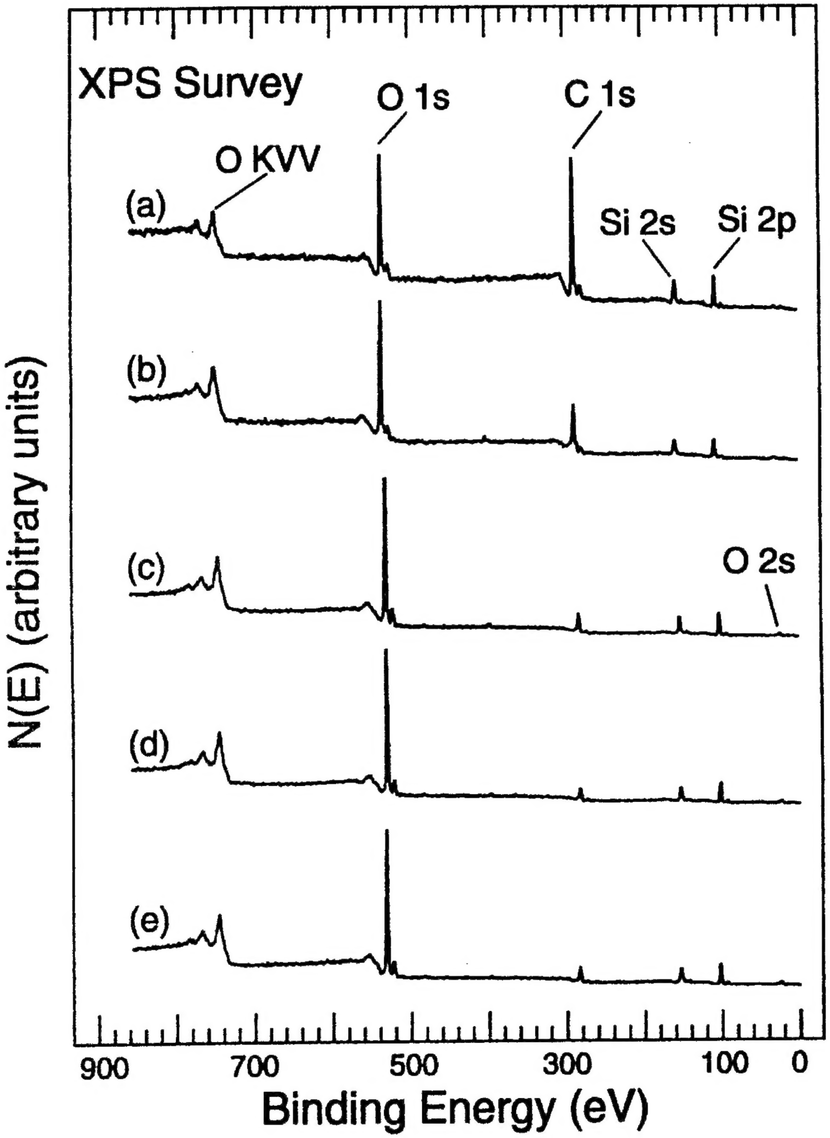
- Generation I POSS lube Delivered –> poor thermal stability
- Generation II POSS lube –> exceeded temperature stability of Ester base stock, and met or exceeded first round of wear tests (static coking tests, three ball and disc)

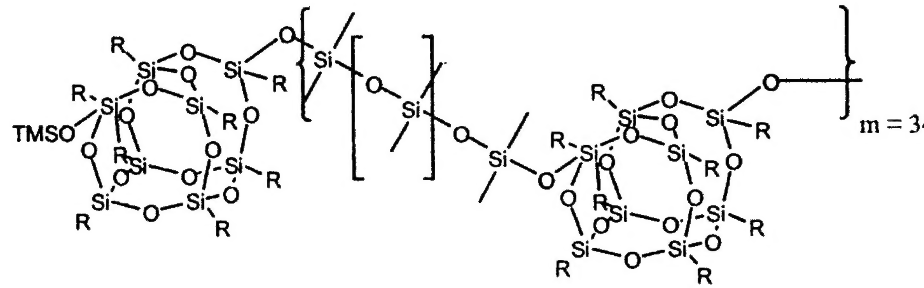
FY00 Objectives:

- Develop methodology for controlling viscosity (altering R groups)
- Determine additives needed to prevent decomposition to grit
- Perform rheological studies (viscosity, shear, stress-strain)
- Send limited samples to PRSL for further testing (static coking, 3-ball/disk)
- Select three best candidates for scale-up

Tasks/Schedules:







POSS-PDMS copolymers

Wt. % of Element

Exposure	O	C	Si
As entered	18.1	64.1	17.8
2-h	38.0	41.3	20.7
24-h	47.6	23.7	28.6
63-h	54.0	13.5	32.5
4.75-h air	54.6	18.1	27.3

Goal: Develop Multi-Functional, Space-Resistant Materials

Satellites & Space Systems

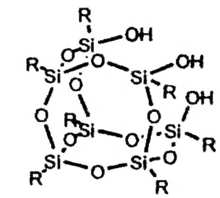
Bond	Dissociation Energy (EV)	λ (nm)	Material
$-C_6H_4-C(=O)-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

Objectives

- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials by 10x

- Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation

POSS R&D Summary



6.1/AFOSR — **NWV/AFOSR** — **6.2/AFRL**

Monomers & Polymers Research

- Fundamental studies ---> polymer property understanding (cage size, POSS miscibility, polymer type).
- Polymer Processing ---> reactive processing, polymer blends, composites
- Center of Excellence on POSS polymer research

Applications Research

- Lightweight, low-cost, high-temperature, high-strength
- Utilize economical small-scale SRM insulation screening for large scale testing
- Apply basic R&D work on POSS blends to POSS lubes to meet Phase III IHPTET Goals
- Initial work on space-resistant polymers is remarkable

Multi-Functional, Space-Resistant Materials

FY99 Accomplishments:

- **Collaboration with Prof. Gar Hoflund (U of Florida) for AO testing**
- **Synthesis of POSS-PDMS copolymer and thin-film casting**
- **AO testing of POSS-PDMS polymer →** Formation of protective layer, VUV resistance, Self-annealing!!
- **Synthesis of POSS-polyurethane of 20 and 60 wt. %**
- **Collaboration with JPL on POSS-epoxies**

FY00 Goals:

- **Synthesis & testing of nanocomposites (POSS-polyurethanes, POSS-polyimides, POSS-epoxies, Clay-Nylons)**
- **Incorporation of POSS into JPL space-epoxies**
- **Publications & Presentations!!**
- **Modeling of multiple source space damage**
- **Develop collaboration with VS**